Supporting Information

Ultrasonication-induced Co-based metal–organic frameworks nanoparticle for red light photocatalytic aerobic oxidation

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Experimental Section

Materials and Measurements.

All reagents and solvents are commercially available (Beijing innoChem Science & Technology Co. Ltd.), and they were further dried by the vacuum rotary evaporator to remove all traces of water and then stored in the air-filled glovebox. The 15 mL Schlenk tube charged with a magnetic stirrer, which was used as the reactor in the thioether oxidation and benzyl alcohol dehydrogenation reactions. The light was provided by a 30 W red LED light.

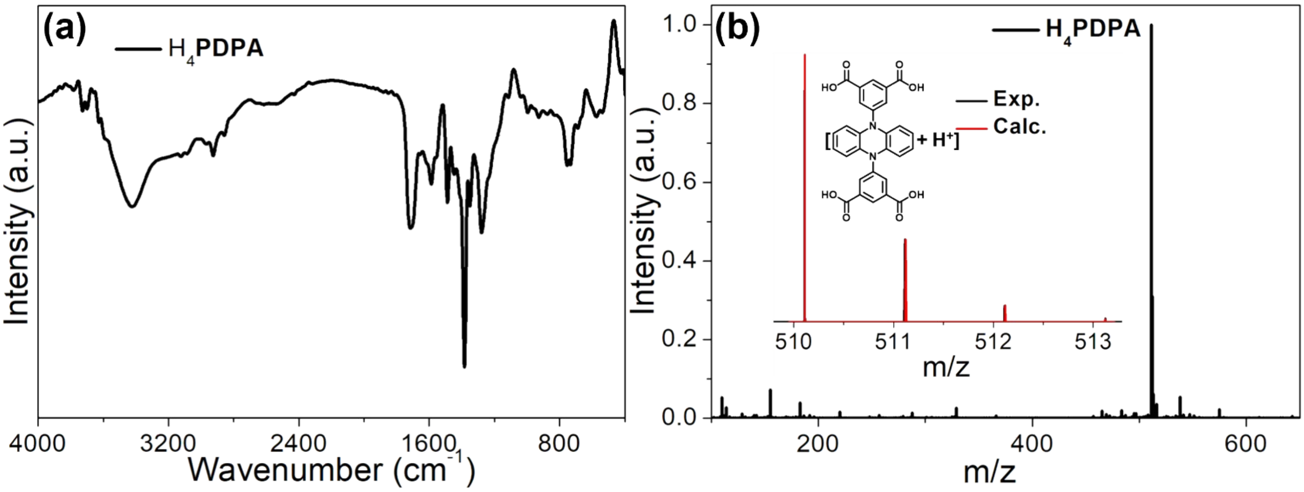
The chemical structures of the products were confirmed by comparison with standard chemicals and GC-MS (Agilent Technologies, GC 7890B, MS 5977A) data. GC equipped with a FID detector (Agilent Technologies, GC 7890 B) and a HP-5 5% phenyl methyl siloxane column (30m × 0.32mm × 0.5 μm), which was used for the quantifiable measure of N-phenylmorpholine. The size and morphology of catalysts were measured by a Hitachi New Generation SU8010 field emission scanning electron microscope (FE-SEM, JSM-670 F). The transmission electron microscopy (TEM) images, high-resolution transmission electron microscopy (HRTEM) images (with an acceleration voltage of 200 kV), and selected area fast Fourier transform (FFT) pattern were measured on a JEOL JEM-3000F microscope, which with a CCD camera as the detector. A Varian Cary 500 UV-Vis spectrophotometer was used to record the UV-Vis diffuse reflectance spectra (DRS) of various solid samples. The photoelectrochemical characterization was performed on a Metrohm-Autolab AUT302N Electrochemical workstation. Photocurrent measurements were carried out in a typical three-electrode configuration with an Ag/AgCl electrode, a coiled Pt wire as the reference and counter electrode, respectively. X-ray diffraction (XRD) studies of catalyst were carried out with a Rigaku instrument. The electron paramagnetic resonance (EPR) experiments were carried out on Bruker A300 instrument operating in the X-band at room temperature.

Single-crystal X-ray crystallography.

Diffraction data for all complexes were measured on a Rigaku instrument (Cu Kα radiation) in Φ and ω scan modes. All structures were solved by direct methods, followed by difference Fourier syntheses, and then refined by full-matrix least-squares techniques on F^2 using SHELXL.[1] All other non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in the calculated position and refined in the isotropic direction using a riding model. Although the positions of hydrogen atoms in the organic framework are calculated based on standard bonding geometries, the hydrogen atoms in water molecules are placed based on idealized water geometry due to the challenges in their direct observation. Table S1 summarizes X-ray crystallographic data and refinement details for the complexes. The CCDC reference number is 2446145 for **XAIU-4**.

Synthesis of $\mathrm{H_4PDPA}$.[2] A suspension of 5,10-dihydrophenazine (1.00 g, 5.50 mmol), dimethyl 5-iodoisophthalate (4.40 g, 13.75 mmol), RuPhos (103 mg, 0.22 mmol), the corresponding precatalyst (180 mg, 0.22 mmol) and NaOtBu (2.11 g, 22.00 mmol) in anhydrous 1,4-dioxane (30 mL) was subjected to three consecutive freeze–pump–thaw cycles to ensure complete inertisation. The sealed reaction vessel was then stirred and maintained at 110 °C for 12 h. After cooling to ambient temperature, the reaction mixture was diluted with $\mathrm{CH_2Cl_2}$ (100 mL) and the organic layer was separated. The aqueous phase was further extracted with $\mathrm{CH_2Cl_2}$ (2 × 100 mL), and the combined organic extracts were washed with brine (3 × 50 mL), dried over anhydrous $\mathrm{Na_2SO_4}$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to furnish the $\mathrm{Me_4PDPA}$ ligand as a red crystalline solid (2.21 g, 3.90 mmol, 65 %).

$\mathrm{H_4PDPA}$ was prepared by stoichiometric base-promoted hydrolysis of its tetramethyl ester under strictly inert conditions. A round-bottom flask charged with $\mathrm{Me_4PDPA}$ (0.113 g, 0.20 mmol) was evacuated and back-filled with $\mathrm{N_2}$ (3 cycles), after which degassed THF/MeOH (1:1 v/v, 20 mL) was added to give a homogeneous solution. A deoxygenated aqueous NaOH solution (1 M, 8 mL) was introduced drop-wise via syringe pump over 10 min at 25 °C. The resulting mixture was then heated at reflux (100 °C) for 16 h under a static $\mathrm{N_2}$ atmosphere. Volatile organics were removed under reduced pressure, and the residual aqueous phase was acidified to pH 5–6 with concentrated HCl (12 M). The orange-red solid was collected by filtration, washed thoroughly with degassed $\mathrm{H_2O}$, and dried in vacuo (95 mg, 0.186 mmol, 90 %). The free acid $\mathrm{H_4PDPA}$ is air-sensitive and should be stored under $\mathrm{N_2}$ at –20 °C to suppress oxidative degradation. Infrared spectroscopy (IR) of $\mathrm{H_4PDPA}$ (Scheme 1a): 3421 (*m*), 2925 (*w*), 1710 (*w*), 1587 (*s*), 1488 (*s*), 1384 (*s*), 1278 (*m*), 991 (*w*), 931 (*s*),754 (*s*), 576 (*w*). The ESI-HRMS spectrum of the final ligand exhibited the expected peak of $[\mathrm{MW+H}]^+$ at m/z = 510.10 in positive mode (Scheme 1b).



Scheme 1. (a) IR data of $\mathrm{H_4PDPA}$ ligand; (b) ESI-HRMS spectrum of $\mathrm{H_4PDPA}$ ligand.

[1] G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, **2015**, *71*, 3-8.

[2] Y. Shi, P. Wang, M. Li, T. Zhang, G. Han, C. Duan, *Angew. Chem. Int. Ed.*, **2023**, *62*, e202219172.

Table S1. Crystallographic data of **XAIU-4**.

Complex	**XAIU-4**
Formula	$C_{16}H_{21}CoNO_9$
Formula weight	430.280
T (K)	293 (2)
Crystal system	Monoclinic
Colour	Brown
Shape	Needle-shaped
Space group	$P2_1/c$
a (Å)	5.3542 (2)
b (Å)	33.0648 (11)
c (Å)	10.7480 (5)
α (°)	90
β (°)	96.150 (4)
γ (°)	90
V (Å^3)	1891.83 (13)
Z	4
D_c(g cm^{-3})	1.511
μ (mm^{-1})	7.567
Reflns coll.	12239
Unique reflns	3685
R_{int}	0.0460
$^aR_1[I \geq 2\sigma(I)]$	0.0766
$^bwR_2$(all data)	0.2243
GOF	1.0245

$^aR_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $^bwR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2. Selected bond lengths (Å) and angles (°) of **XAIU-4**.

Bond lengths (Å)					
Co1—O1	2.078 (3)	Co1—O5	2.138 (4)	Co1—O7	2.185 (4)
Co1—O3^i	2.064 (3)	Co1—O6	2.081 (3)	Co1—O8	2.089 (3)
Bond angles (°)					
O3^i—Co1—O1	179.18 (15)	O6—Co1—O5	88.36 (14)	O8—Co1—O1	88.71 (12)
O5—Co1—O1	87.53 (18)	O7—Co1—O1	94.27 (18)	O8—Co1—O3^i	91.82 (13)

O5—Co1—O3^{i}	91.84 (19)	O7—Co1—O3^{i}	86.37 (19)	O8—Co1—O5	90.81 (15)
O6—Co1—O1	92.54 (12)	O7—Co1—O5	178.21 (15)	O8—Co1—O6	178.47 (12)
O6—Co1—O3^{i}	86.92 (12)	O7—Co1—O6	91.49 (13)	O8—Co1—O7	89.29 (14)
Symmetry codes: (i) *x*+1, -*y*+1/2, *z*-1/2; (ii) -*x*+1, -*y*+1, -*z*+1; (iii) *x*-1, -*y*+1/2, *z*+1/2.					

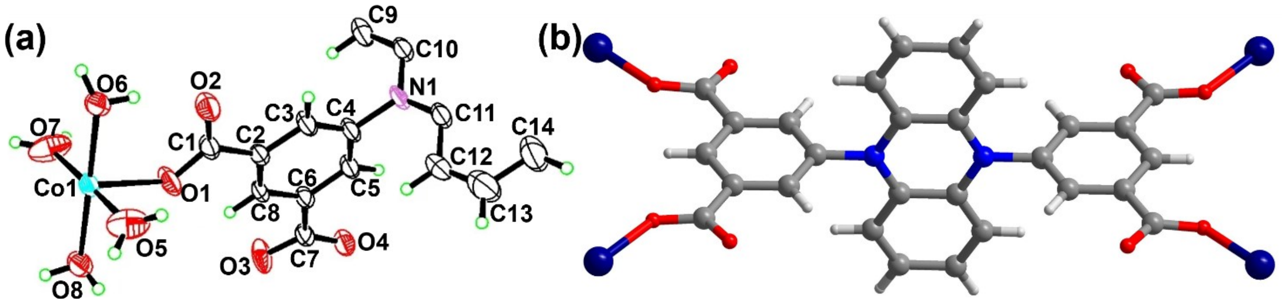


Figure S1. (a) The ADP image of structure; (b) The coordinated mode for **PDPA**$^{4-}$ ligand for **XAIU-4**.

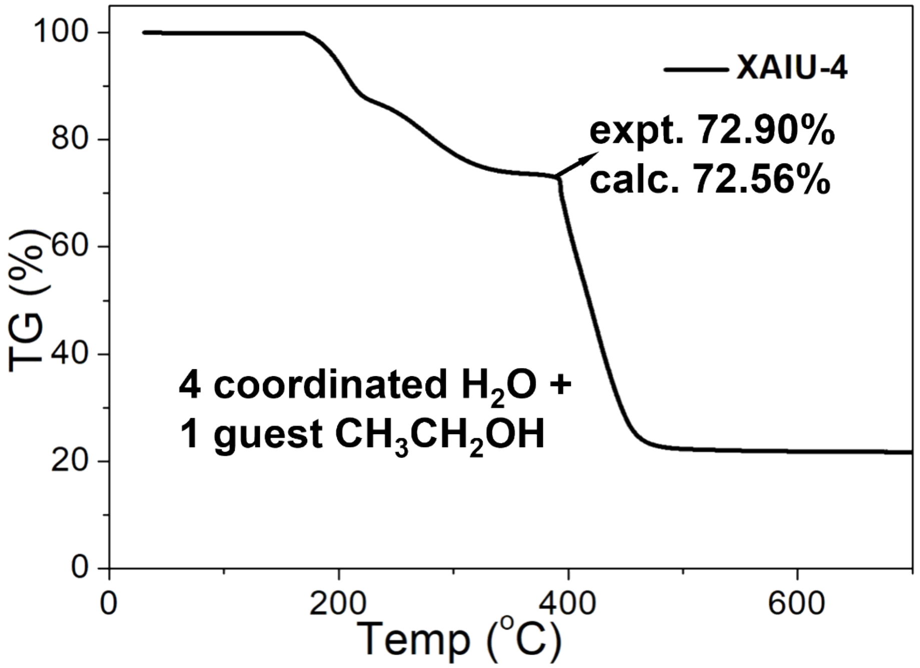


Figure S2. N_2 sorption isotherms at 77 K of **XAIU-4**.

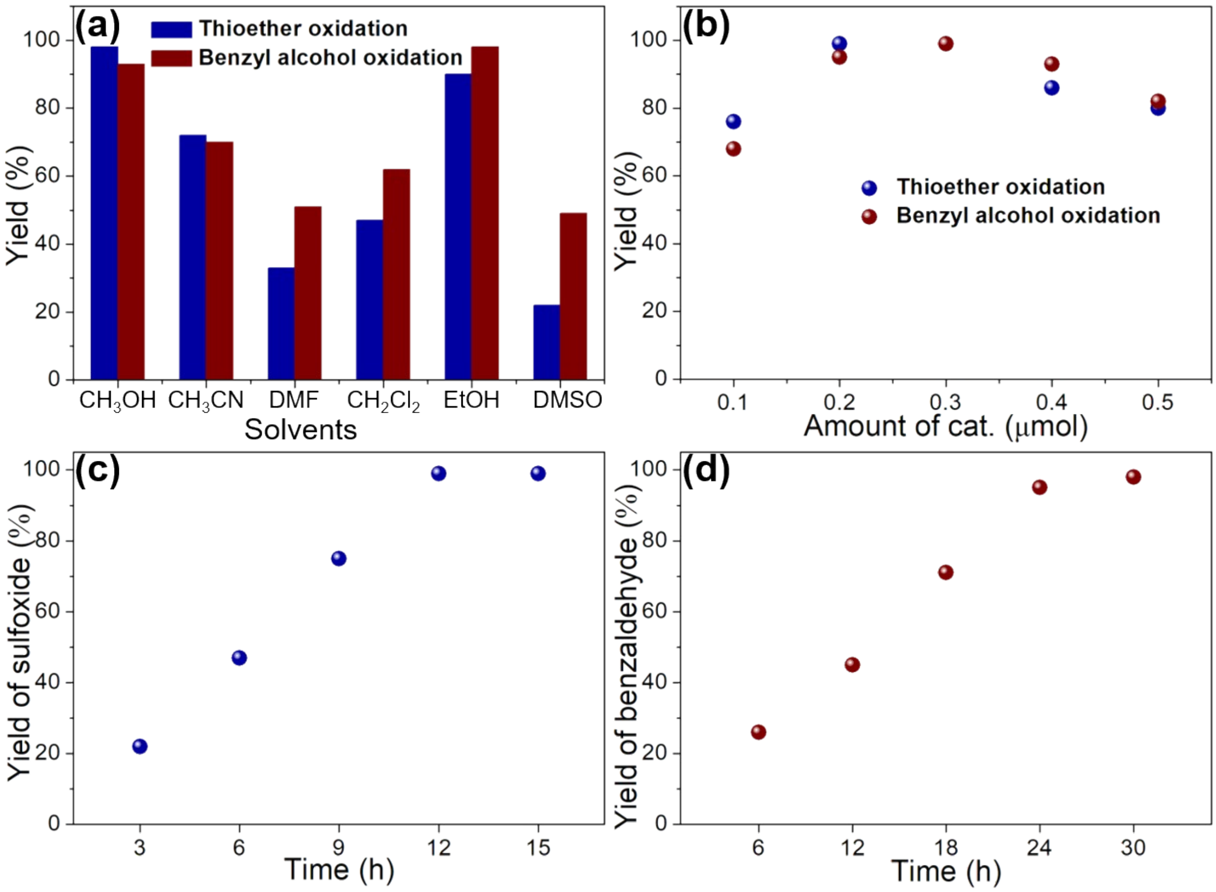


Figure S3. (a) Yields of sulfoxide and benzaldehyde in different solvents; (b) the influence of photocatalyst amounts in photocatalytic reactions; the influence of irradiation time on the yield of sulfoxide (c) and benzaldehyde (d) of **XAIU-4**.

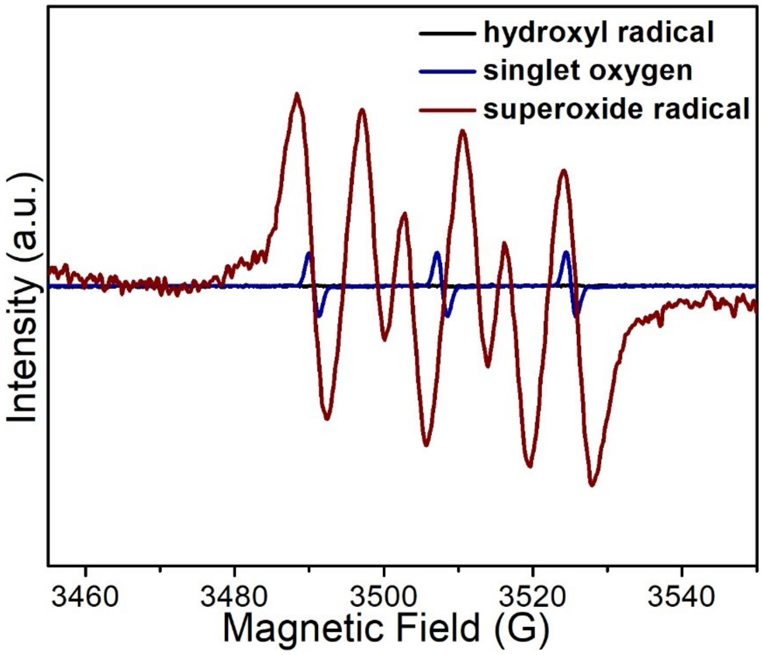


Figure S4. EPR spectra peak of $O_2^{\bullet-}$ or •OH radicals trapped by DMPO, and $^1O_2$ trapped by 2,2,6,6-

Tetramethylpiperidine (TEMP) over **XAIU-4-NP**.